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54 Title: **Stainless steel hardenable by heat treatment**

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This invention relates to stainless steel hardenable by heat treatment, which contains specific proportions of nitrogen and niobium-tantalum in addition to chromium and carbon, and in which any molybdenum and/or tungsten present are kept to a critically low level.

The inventive steel is characterized by the fact that it contains 0.01 to 0.25% carbon, 10 to 16% chromium, 0.04 to 0.2% nitrogen and 0.03 to 0.75% niobium or niobium and tantalum, whereby the steel should preferably not contain more than 0.3% molybdenum, not more than 0.5% tungsten and not more than 0.5% molybdenum and tungsten on aggregate, and preferably up to 0.75% vanadium.

The steel is made particularly in the form of bar, from which various products are made. In particular, the invention relates to use of the steel to make blades for turbines and compressors, characterized by the fact that the blades are made of a steel containing 0.01 to 0.25% carbon, 0.01 to 3% manganese, 0.01 to 2% silicon, 10 to 13% chromium, 0.04 to 0.16% nitrogen, 0.03 to 0.75% niobium or niobium and

tantalum, and the remainder of which consists principally of iron and preferably contains not more than 0.3% molybdenum, not more than 0.5% tungsten, not more than 0.5% molybdenum and tungsten on aggregate and preferably up to 0.75% vanadium.

The invention concerns rustproof, pure qualities of chromium steel, particularly the A.I.S.I. (American Iron & Steel Institute) 400 range of steels, the composition of which is stated under "general".

One of the objects of the invention is the creation of a creep-resistant stainless steel, hardenable by heat treatment, producing high tensile strength and a high yield point at both room temperature and a higher temperature and which is also ductile and deformable and has good impact resistance.

An additional object is the creation of such a steel which responds well to hot working, e.g. in the production of plate, sheet, strip, bar, rod and wire, and which is suitable for the widest variety of working and forming methods, e.g. chip removal, cropping, blanking out, thread cutting, forging, etc and which can also easily be soldered, brazed and welded, e.g. to make the widest possible range of products suitable for applications in which temperatures of up to 595°C are reached.

Another object is the creation of a stainless steel and a process for its heat treatment in which the metal reacts consistently throughout to the heat treatment and the stainless steel displays a high resistance to tempering and good long-term creep stability.

In general, the invention is based upon the combination of chemical elements, the composition of constituents and the relationship of each of them to one or more of the others and on the sequence of stages and the reciprocal relationships between them, as described below.

For a better appreciation of certain characteristics of the invention, it is stated at this point that the pure stainless chromium steel qualities hardenable by heat treatment, i.e. the A.I.S.I 400 range of steels from 403 to 440, have a martensitic structure. This range includes type 403 (11.5 to 13.5% chromium, max. 1.00% manganese, max. 0.50% silicon, max. 0.15% carbon and the remainder iron), type 410 (11.5 to 13% chromium, max. 1.00% manganese, max. 1.00% silicon, max. 0.15% carbon and the remainder iron), type 414 (11.5 to 13.5% chromium, 1.25 to 2.50% nickel, max. 1.00% manganese, max. 1.00% silicon, max. 0.15% carbon and the rest iron), type 416 (12 to 14% chromium, 1.25% manganese, max. 1.00% silicon, min. 0.15% sulphur, up to a maximum of 0.60% each of molybdenum and zirconium, max. 0.15% carbon and the remainder iron), type 420 (12 to 14% chromium, max. 1.00% manganese, max. 1.00% silicon, over 0.15% carbon and the remainder iron), type 431 (15 to 17% chromium, 1.25 to 2.50% nickel, max. 1.00% manganese, max. 1.00% silicon, max. 0.20% carbon and the remainder iron) and type 440 (16 to 18% chromium, max. 1.00% manganese, max. 1.00% silicon, whereby levels of a maximum of 0.75% molybdenum and 0.60 to 1.20% carbon are specified for various derivatives of type 440, and the remainder iron).

Although the stainless steels hardenable by heat treatment in range 400 have many

favorable properties and are suitable for the widest possible range of applications, as aforementioned, it has emerged that they leave much to be desired in various respects and that they are not really suitable for certain applications. These known steels are susceptible to pronounced segregation symptoms, have insufficient ductility, restricted suitability for chip removal and are susceptible to stress corrosion cracking. In particular, these steels tend to have an inconsistent microstructure and low physical strength due to solid carbide segregation. These steels are also susceptible to heat treatment cracking.

Although stainless pure chromium steels have been modified by the addition of one or more additional constituents such as molybdenum, tungsten, vanadium and niobium in recent years, no desirable combination of strength at both room and high temperatures with ductility has yet been wholly achieved. Reference is made to the modifications which have been made over the years with the stainless steel quality with 12% chromium. Initially, as aforementioned, this steel, designated type 410, had the following analysis: 11.5 to 13.5% chromium, a maximum of up to 1.00% each of manganese and silicon, a maximum of 0.15% carbon and the remainder principally of iron. The steel was subsequently modified by the addition of small quantities of the constituents nickel, molybdenum, tungsten and vanadium and designated type 422, which has the following analysis in a typical case: 13.0% chromium, 0.75% nickel, 1.0% molybdenum, 1.0% tungsten, 0.34% vanadium, 0.22% carbon and the remainder iron. A further modified steel, generally designated 12 Cr-Ni-Mo-V, has the following typical analysis: 11.5% chromium, 0.70% nickel, 1.0% molybdenum, 0.25% vanadium, 0.17% carbon and the remainder iron. A further modified steel, designated 12-2W, has the analysis: 12.0% chromium, 2.0% nickel, 3.0% tungsten, 0.18% carbon and the remainder iron. However, it has emerged that the desired combination of strength and ductility is absent from these various modified steels. They lack the combination of strength at room temperature with strength at high temperature. If one is sufficient, the other is deficient. In addition, they lack ductility and their impact resistance and resistance to stress corrosion cracking are insufficient. They are susceptible to notching. Moreover, they are expensive because of the considerable addition of nickel, molybdenum and tungsten.

The most recent modified type 410 stainless steel which was made available is perhaps that described in US patent specification 3 000 729. This steel contains 0.05% to 0.35% niobium-tantalum with or without up to 0.20% vanadium, in addition to approximately 10.0 to 14.0% chromium and 0.07 to 0.14% carbon. The remainder of the steel consists, of course, mainly of iron. Although this steel has many of the properties currently desired, it lacks strength both at room and raised temperatures. Moreover, the desired strength is not achieved merely by adding a larger quantity of the niobium-tantalum and vanadium constituents.

Another such steel is described in US patent specification 3 139 337. However, the tensile strength is also insufficient in this case. Moreover, the impact resistance is lacking. Like various steels of the qualities mentioned above, this steel is impermissibly expensive, due to the type and quantity of the alloying additives used.

One of the advantages of this invention is thus the creation of a steel which does not possess the shortcomings of the known steels, which is a comparatively cheap, modified, stainless, pure chromium steel hardenable by heat treatment, which is

moreover suitable for hardening and tempering, forming a steel which is strong, ductile and resistant to stress corrosion cracking both at room temperature and at high temperatures, which can easily be cut and worked, e.g. by cropping, blanking out, thread cutting, etc and which can also easily be soldered, brazed and welded, as desired to make the widest possible range of items or finished products, and which can be subjected to heat treatment simply and directly, producing consistent, reproducible results.

As far as practical implementation of the invention is concerned, it is known that strength and hardness of state-of-the-art steels have been developed thanks to the considerable carbon content. The steels are naturally martensitic in their hardened state. Solid ledeburitic carbides are formed in the ingot in state-of-the-art steels. These carbides are retained as segregations which cannot be dispersed easily into the base steel material either by working (with deformation) or heat treatment. On the contrary, they persist as clusters or linear inclusions (straightened fibers) after the ingot has been converted into semi-finished products (steel sections) or the final product. The metal is consequently weakened, particularly transversely, i.e. at right angles to the direction of rolling or drawing.

Whilst greater strength of certain state-of-the-art steels can be achieved in the by the addition of molybdenum and/or tungsten, the addition of one or both of these constituents reduces the solubility of carbon considerably, i.e. it is difficult to make carbon dissolve and difficult to achieve a desired quenching hardness which is retained after tempering. Moreover, the molybdenum carbide and tungsten carbide which form have, like the chromium carbide, a tendency to flow together or enlarge, producing the solid carbides dispersed throughout the entire metal. It is assumed that these solid carbides necessarily affect deformability and ductility, although they prevent the metal from yielding under stress and make it stronger in a certain sense. This effect is not a genuine hardening and strengthening effect, but instead represents a type of yield prevention, introduced deliberately. In particular, further increases in the carbon, molybdenum and tungsten content will not fully achieve an increase in hardness and strength at high temperature, because it becomes more difficult to dissolve the carbon in the larger carbides. It is also more difficult to work the metal in a rolling mill as the carbon content increases.

However, apart from the theory, it has been found that state-of-the-art steels which contain molybdenum and/or tungsten, or even chromium, in combination with considerable quantities of carbon, do not display a combination of deformability and ductility with tensile strength.

It has now been found that a secondary hardening effect, beyond the hardening achieved with carbon, can be achieved by the inventive addition of nitrogen and niobium-tantalum in the so-called pure chromium steels. Conversion evidently takes place between nitrogen and niobium-tantalum, which is highly favorable to achieving a fine-grain structure in which the nitrides are dispersed throughout the entire metal, making the base mass stronger. An increase in hardness and strength results, not only at room temperature, but also at increased temperatures. This is achieved in the absence of solid carbides, as it has been found that the presence of niobium-tantalum reduces the formation of solid chromium carbides to a minimum. The chromium carbides which nevertheless form are small and very well dispersed

through the steel. They have a direct beneficial effect on deformability and ductility.

As it appears that conversion with carbon is more beneficial than conversion with nitrogen, it is not desirable that a large quantity of carbon be present to achieve the best results, but only that as much carbon be used as necessary to achieve the desired quenching hardness. Larger quantities of carbon will only combine with one of the alloying additives present, such as niobium-tantalum, chromium and others, directly reducing the effect thereof. Moreover, the carbides which form are undesirable inclusions which reduce deformability and ductility.

Nitrogen is used in a quantity sufficient to achieve the desired final hardness and retain it during tempering. The addition of nitrogen achieves hardness and strength, subsequently retaining them at increased temperatures. It appears that a certain molecular interlocking takes place, instead of the restrictive effect detected with the solid carbides present in the state-of-the-art steels. In any case, apart from the theory, deformability and ductility are obtained in the inventive steel, as well as hardness and strength. Hardness and strength are further enhanced by the addition of a controlled quantity of vanadium, as will be demonstrated below, without a loss of deformability and ductility.

The principal constituents of the inventive stainless steel are approximately 0.01 to 0.25% carbon, approximately 0.01% to 3% manganese, approximately 0.01 to approximately 2% silicon, approximately 10% to approximately 16% chromium, whereby any molybdenum and any tungsten present do not exceed 0.3% and 0.5% respectively or 0.5% on aggregate, additionally approximately 0.04 to approximately 0.2% nitrogen, approximately 0.03% to approximately 0.75% niobium-tantalum, up to approximately 0.75% vanadium and the rest predominantly only iron. Nickel may be present in quantities of up to a maximum of 2%. The constituents phosphorous and sulphur which are usually present in all stainless steels are restricted to quantities which do not exceed a maximum of 0.050% respectively. Any molybdenum present is held to a level which does not exceed 0.3% and preferably approximately 0.2%, due to the ferrite-forming tendency, as will be explained in more detail below. Accordingly, any tungsten present is kept to a level which does not exceed approximately 0.5%, preferably 0.2%, in order to achieve the best results. The aggregate content of molybdenum and tungsten is kept to a level which does not exceed approximately 0.5% and preferably to a level which does not exceed 0.2%, preferably to achieve optimum deformability and ductility in a steel at the lowest possible price. In fact, molybdenum and tungsten seldom exceed levels of 0.05 to 0.08% for molybdenum and approximately 0.10% for tungsten.

Vanadium is added in a quantity of up to approximately 0.75%, as will be explained below. The vanadium content usually amounts to approximately 0.03 to 0.75%, preferably approximately 0.30 to approximately 0.35% or approximately 0.03 to 0.35% in particular, if the best combination of hardness, strength and ductility is to be achieved.

The constituents carbon, chromium, nitrogen and niobium-tantalum are of crucial significance in every sense in the inventive steel. The chromium content must be at least 10%, as a steep fall in resistance to corrosion and an undesirable development of scale will otherwise occur in use at increased temperatures. Moreover, a loss of

solubility of nitrogen, which is an absolutely necessary constituent of steel, occurs. On the other hand, the chromium content should not exceed approximately 16%, because a chromium content above this level creates a tendency for a steel to form which is disproportionately ferritic, which is associated with a decline in physical properties. The preferred chromium content of a steel at the lowest price is approximately 11 to 12% or even approximately 10 to approximately 13%. The chromium content of a steel with greater strength, ductility and greater resistance to corrosion is approximately 13 to 15%, particularly approximately 15%.

The carbon content of the inventive stainless steel is held at a level of at least 0.01%, as only minor advantages can be gained from a lower level. However, the carbon content must not exceed approximately 0.25% because, as has been found, a greater quantity of carbon leads to the development of a disproportionate number of segregations, which have a negative influence on the ductility of the metal. A preferred carbon content is approximately 0.15 to 0.25%, particularly 0.1 to approximately 0.2% for certain applications, particularly turbine and compressor blades. In certain applications, such as steels for general use, a carbon content of approximately 0.05 to approximately 0.15% is preferred for steels with a higher chromium content. In other steels again, such as those in which greater hardness is required, a carbon content of approximately 0.10 to approximately 0.20% is preferred.

The nitrogen component is, as aforementioned, absolutely necessary, in a quantity of approximately 0.04 to approximately 0.2%. It has been found that a nitrogen content lower than 0.04% has no particular advantages. If the nitrogen content exceeds approximately 0.2%, there is a possibility that a defective metal will be obtained, due to the high gas content, even with a chromium content as high as approximately 16%. In general, a nitrogen content of approximately 0.06 to 0.16% is preferred, although the nitrogen content is 0.04 to 0.2% in certain embodiments, as stated below.

As aforementioned, niobium-tantalum is present in a quantity of approximately 0.03 to approximately 0.75%. At least 0.03% niobium-tantalum is required to achieve any advantage either in respect of grain size control or conversion with the nitrogen present. A niobium-tantalum content of over 0.35% will only bind carbon, reducing the soluble quantity, so that both the quenching hardness and the tempering hardness suffer. Moreover, a disproportionate quantity of niobium-tantalum causes solid segregations, which affect the deformability and ductility of the metal. The preferred niobium-tantalum content for most steels is in the range of approximately 0.1 to 0.3% or even approximately 0.1 to approximately 0.2%, or particularly 0.08 to 0.15%, depending upon the ratios of the other constituents, as will be explained in more detail below.

If vanadium is used, it is present in a quantity of at least 0.03%, as any smaller quantity offers little or no benefit. However, the vanadium content should not exceed approximately 0.75%, as an excess will only bind carbon, like an excess of niobium-tantalum, whereby the soluble quantities will decrease, with a disadvantageous influence on both the quenching hardness and the tempering hardness. Solid segregations also form, causing a fall in the yield point, deformability, ductility and impact resistance. It appears that the niobium-tantalum reacts with the carbon

present whilst the vanadium and nitrogen content produce the best increase in hardness and strength, if both niobium-tantalum and vanadium are present in the steel. The presence of both these constituents gives the steel the best physical properties.

As aforementioned, the constituents manganese, silicon, phosphorous and sulphur, i.e. constituents which are usually present in all stainless steels, are present in this steel. The manganese and silicon content are at least 0.01% each, which practically represents the lower limit for these constituents, and up to approximately 1 or even 2% for the silicon and up to approximately 1% for the manganese. In reality, the manganese, also as aforementioned, can be used advantageously in quantities up to approximately 3%, principally as a stabilizer for the high-temperature austenite of the steel. However, a greater quantity would only make the conversion into martensite in quench hardening of the metal sluggish. Manganese also has the advantage that it serves as a suitable carrier for the introduction of a considerable proportion of the nitrogen required. The nitrogen is generally introduced by using a nitrided electrolytic manganese. The silicon used serves to impart resistance to the formation of scale in high-temperature applications. Silicon in a quantity in excess of 2% causes segregation and has a very similar effect to an excess of carbon in this respect. Moreover, superfluous silicon tends to render the metal inadmissibly ferritic.

The phosphorous and sulphur content should not exceed a maximum level of 0.05% each, as they have a tendency to cause difficulties in hot working or hot deforming. Moreover, the impact resistance of the metal is drastically reduced by higher sulphur contents.

As aforementioned, the nickel content of the steel should not exceed 2%, because nickel is an austenite stabilizer and hinders the tempering of the metal if present in high quantities. Moreover, nickel is an expensive constituent. Steel has a preferable nickel content which does not exceed a maximum of 1% and preferably a maximum of 0.5%.

An important feature of the inventive steel is that it is largely free of the constituents molybdenum and tungsten, which are generally present in considerable quantities in state-of-the-art creep-resistant, stainless pure chromium steels. It has been found that both these constituents encourage the development of hypereutectoid steel and the formation of massive segregations. Although both molybdenum and tungsten have long been regarded as powerful carbide-forming elements which impart strength at high temperatures, it has emerged that the carbides of both these constituents are unsuitable for the purposes of the invention, possibly due to their tendency to create solid carbide segregations, because they clearly affect deformability, ductility and impact resistance. This effect is attributed to interference with the plastic flow. However, apart from the theory, it has been found that solid carbides are, in fact, present. In the inventive steel, the quantity of any molybdenum present is intentionally restricted to a level which does not exceed approximately 0.3%, preferably 0.2%, and the quantity of any tungsten present in the metal is restricted to a level which does not exceed approximately 0.5%, preferably 0.3%, whereby the aggregate of these two constituents does not exceed approximately 0.5%, preferably approximately 0.2%.

A preferred inventive steel consists of the principal constituents approximately 0.01 or even approximately 0.05 to approximately 0.25% carbon, approximately 0.01 to approximately 1% manganese, approximately 10 to approximately 13% chromium, approximately 0.04 to 0.16 or even approximately 0.2% nitrogen, approximately 0.03 to approximately 0.75 or preferably approximately 0.1 to approximately 0.3% niobium-tantalum, up to approximately 0.75, preferably approximately 0.03 to approximately 0.75% vanadium, whereby the aggregate of all the molybdenum and tungsten present does not exceed approximately 0.5%, preferably approximately 0.2% as a maximum level, and the rest principally iron. Another steel consists of the principal constituents of approximately 0.01 to approximately 0.2% carbon, approximately 11 to approximately 12% chromium, approximately 0.04 to 0.16% nitrogen, approximately 0.1 to approximately 0.75 or preferably approximately 0.1 to 0.3% niobium-tantalum, approximately 0 to approximately 0.50% vanadium, whereby the vanadium content is preferably approximately 0.2% to approximately 0.4% and the aggregate of any molybdenum and tungsten present does not exceed approximately 0.5%, preferably approximately 0.2%, and the rest principally iron. Another steel, which is particularly suitable for refining petroleum and chemical processes, in which strength, ductility and resistance to softening at high temperatures are necessary, consists of the principal constituents of approximately 0.1 to approximately 0.2% carbon, approximately 13 to approximately 15% chromium, approximately 0.04 to approximately 0.2% nitrogen, approximately 0.1 to approximately 0.3% niobium-tantalum and 0 to 0.6%, preferably approximately 0.2 to 0.6% vanadium, whereby the aggregate of any molybdenum and tungsten present does not exceed approximately 0.5%, preferably approximately 0.2%, whereby the remainder is principally iron.

The inventive stainless steel can be melted practically in an arc furnace. However, it can also be melted in an induction furnace if required. Of course, it can also be melted in a vacuum, i.e. in a vacuum in an arc furnace. Finally, a double melting process may be used, i.e. melting in an arc or induction furnace followed by remelting in a vacuum. However, melting in an arc furnace is generally wholly satisfactory for producing a satisfactory steel with the lowest overheads.

However the steel is melted, it is practically cast in the form of crude ingots, which are supplied as slab, rolled billets or billets, which are then further converted into plate, sheet, bar or wire by ordinary hot rolling. The metal can easily be forged, as in the production of the widest variety of crudely formed items, then cut to the specified dimensions.

The steel is particularly suitable for the production of steam turbine blades or compressor blades for jet engines. Due to its high yield point, the steel permits the construction and use of larger blades and thus enhanced performance by turbines and compressors in operation.

The inventive stainless steel and artifacts are hardened by quenching, e.g. by heating to a temperature of approximately 925 to 1150°C for a period of up to four hours or more, with subsequent quenching in air, oil, water or similar. Following quench hardening the metal may be subjected to tempering, to relieve stresses and achieve the desired level of hardness. For this purpose the metal is heated again to a temperature of approximately 480 to 705°C and cooled as desired. This treatment

achieves an excellent combination of yield point, deformability and ductility, as stated in more detail below. Yield points of 8790 kg/cm² and higher are achieved with a Charpy notched bar impact strength of at least 2.5 to 2.8 mkg in the hardened, tempered inventive steel.

The surprising properties which are obtained in the inventive stainless steels by the combination of niobium-tantalum and nitrogen with and without vanadium can perhaps best be explained by a comparison with steels in which one or more of these constituents are absent. Table I shows the chemical composition of five stainless 12-chrome steels, namely an inventive steel which contains a combination of the constituents niobium-tantalum and nitrogen. Another inventive steel contains vanadium and three other steels, which differ from the inventive steels by the absence of one or both of the constituents niobium-tantalum and nitrogen. Table II shows the Rockwell hardness of these different steels after heating and quenching, on the basis of different temperatures and also after tempering of the various hardened steels.

Table I

Chemical composition of five stainless 12-chromium steels											
{PRIVATE }Melt no.	C	Mn	P	S	Si	Cr	Ni	Mo	N	Nb**)	V
R 4982-1	0.049	0.74	0.015	0.017	0.33	12.25	0.13	0.04	0.058	0.005	0.01
R 4982-2*)	0.049	0.74	0.015	0.017	0.33	12.25	0.13	0.04	0.058	0.11	0.01
R 4982-3*)	0.049	0.74	0.015	0.017	0.33	12.25	0.13	0.04	0.058	0.11	0.21
12 Cr-Cb	0.12	0.30	0.015	0.016	0.28	12.00	0.15	0.04	0.027	0.15	0.01
12 Cr-Cb-V	0.13	0.43	0.011	0.019	0.20	11.67	0.16	0.08	0.026	0.10	0.11

The remainder consists mainly of iron only.

*) Inventive steel

**) Niobium-tantalum, entered as niobium

The steels in Table I were solution-annealed in different ways at 926°C, 982°C and 1038°C, quenched in oil, then tempered at 649°C for four hours and air-cooled. The Rockwell hardness was determined for all the specimens in their quenched and tempered state and is shown in Table II.

Table II

Rockwell hardness levels for the steels in Table I in both their hardened and hardened and tempered states						
Melt no.	926°C Oil quenched	982°C Oil quenched	1038°C Oil quenched	926°C Oil quenched + 649°C/4 hrs air cooled	982°C Oil quenched + 649°C/4 hrs air cooled	1038°C Oil quenched + 649°C/4 hrs air cooled
R 4982-1	C 39	C 38	C 38	B 95	B 95	B 95
R 4982-2*)	C 38	C 38	C 37	C 22	C 24	C 28
R 4982-3*)	C 37	C 38	C 36	C 26	C 27	C 29
12 Cr-Cb	C 42	C 44	C 44	C 23	C 24	C 25
12 Cr-Cb-V	C 43	C 44	C 44	C 23	C 25	C 25

*) Inventive steel

Table I shows that of the various steels of which the chemical composition is stated, those designated 12 Cr-Cb and 12 Cr-Cb-V contain niobium-tantalum or niobium-tantalum and vanadium, whilst their nitrogen content is too low. Whilst the steel designated R 4982-1 indeed contains the constituent nitrogen, it lacks both niobium-tantalum and vanadium. The inventive steels, namely R 4982-2 and R 4982-3 contain both the constituents nitrogen and niobium-tantalum, whereby steel R 4982-3 also contains the constituent vanadium.

As emerges from the figures stated in Table II, all five steels displayed considerable hardness when hardened by quenching, the degrees of hardness lying between Rockwell C 36 and Rockwell C 44. The steels 12 Cr-Cb and 12 Cr-Cb-V display the greatest hardness, namely approximately Rockwell C 44 when quenched at between 982 to 1038°C. This hardness is attributed to the considerable carbon content, namely 0.12 to 0.13%. The three steels R 4982-1, R 4982-2 and R 4982-3 demonstrated hardness from approximately Rockwell C 36 to 38 when hardened by quenching at from 982 to 1038°C, which is attributed to the considerably lower carbon content, namely 0.049%, although a nitrogen content of 0.058% is present, so that the aggregate carbon and nitrogen content of these three steels is 0.107%.

The two steels 12 Cr-Cb and 12 Cr-Cb-V suffer a considerable loss of hardness in their tempered state, the Rockwell hardness falling from C 23 to 25, which corresponds to a loss of about 20 points for each of these steels at the respective hardening temperatures. The steel R 4982-1, which is free of both niobium-tantalum and vanadium but which does contain nitrogen suffers an even greater loss of hardness during tempering, the hardness falling to Rockwell B 95 in this case.

Although considerable hardness is retained by steel R 4982, which contains both nitrogen and niobium-tantalum, the ultimate hardness achieved varies considerably as a function of the hardening temperature, namely from Rockwell C 22 for treatment at 926°C to C 28 for hardening at 1038°C. Only in the steel R 4982-3 containing all three constituents nitrogen, niobium-tantalum and vanadium is the hardness best retained; without taking changes in the heat hardening temperature into account. Whilst this steel has a hardness of Rockwell C 27 after hardening at 982°C and quenching with oil following by tempering, it demonstrates hardness of C 29 after hardening at 1038°C and tempering.

Table III states the chemical composition of five steels and Table IV their comparative physical properties for the purposes of further comparison of the inventive steels with certain of the better state-of-the-art steels.

Table III

Chemical composition of five stainless 12-chromium steels												
Melt no.	C	Mn	P	S	Si	Cr	Ni	Mo	N	Nb**)	V	W
022089*)	0.12	0.85	0.014	0.019	0.23	11.58	0.14	0.03	0.072	0.16	0.25	-
12 Cr-Ni-Mo-V	0.17	0.69	0.016	0.014	0.43	11.71	0.46	1.03	0.032	-	0.19	-
12 Cr-Cb	0.12	0.25	0.014	0.015	0.28	12.0	0.15	0.06	0.019	0.15	<0.01	-
12 Cr-Cb-V	0.13	0.43	0.011	0.019	0.20	11.67	0.16	0.08	0.020	0.10	0.11	-
12 Cr-Ni-	0.23	0.81	-	-	0.28	13.19	0.73	1.03	<0.04	-	0.34	1.11

tungsten, in addition to vanadium and molybdenum. In contrast to these state-of-the-art steels, the preferred inventive steel contains the major constituents of niobium-tantalum and nitrogen as well as vanadium, whilst it is free from the constituents molybdenum and tungsten.

The hardened and tempered inventive steel (melt 033089) has, as shown in Table IV above, a tensile strength of 10 616 kg/cm² at a yield point of 9351 kg/cm², whilst the state-of-the-art steels 12 Cr-Cb and 12 Cr-Cb-V have tensile strengths of 9281 and 9351 kg/cm² respectively and 0.2 limits of only 8156 and 8225 kg/cm² respectively. The state-of-the-art steel 12 Cr-Ni-Mo-V is little better than the two other state-of-the-art steels shown and has a tensile strength of 9843 kg/cm². The superior strength of the preferred steel compared to the three state-of-the-art steels is thus evident.

Although the additional state-of-the-art steel 12 Cr-Ni-Mo-W-V has approximately the same tensile strength and yield point as the preferred steel, namely tensile strength of 10827 kg/cm² and a yield point of 9140 kg/cm² compared to figures of 10 616 kg/cm² and 9351 kg/cm² for this steel, it has been established that the state-of-the-art steel has much poorer deformability and ductility than this steel. Whilst this steel has 16% elongation after fracture at a 60% reduction of area after fracture and a Charpy notched bar impact strength of 3.5 mkg, the state-of-the-art steel demonstrates 17% elongation after fracture at a reduction of area after fracture of only 50% and a Charpy notched bar impact strength of 1.7 mkg. This difference in deformability and strength is even more pronounced if a higher temperature is used for solution annealing. As is evident from Table IV above, the inventive steel has 16% elongation after fracture at a 58% reduction of area after oil quenching at 1093°C and subsequent tempering at 621°C, and a Charpy notched bar impact strength of 2.5 mkg, whilst the best state-of-the-art steel, namely 12 Cr-Ni-Mo-W-V, has an elongation after fracture of 14% at a reduction in area of only 32% and a Charpy notched bar impact strength of only 1.2 mkg if it is treated in the same way. After solution annealing at the higher temperature, the tensile strength and yield point of the inventive steel are superior to those of the known steel. In summary, it may therefore be stated that the tensile strength of the inventive steel is at least equal to the best state-of-the-art steels and superior to them in respect of yield point, deformability and impact strength, by a high margin in the case of the latter.

A further specific example of a preferred inventive steel, melt 3809-2, has the following analysis: carbon 0.16%, manganese 0.02%, phosphorus 0.017%, sulphur 0.016%, silicon 0.10%, chromium 11.18%, nickel 0.19%, molybdenum 0.03%, nitrogen 0.12%, niobium-tantalum 0.09%, vanadium 0.39% and the remainder iron. If hardened by heating to 982°C for 30 minutes, oil-quenching with subsequent tempering at 649°C for four hours and air cooling, this steel has a tensile strength of 9126 kg/cm², an 0.2 limit of 6714 kg/cm², elongation after fracture of 16.7% of the initial length of 5.08 cm, a 53.6% reduction of area after fracture and Rockwell hardness of C 27. If the steel is hardened at the higher temperature of 1038°C for 30 minutes and oil-quenched with subsequent tempering at 649°C for four hours and air cooling, all these physical properties will be improved. The steel treated in this way has a tensile strength of 9977 kg/cm², a yield point of 7221 kg/cm², elongation after fracture of 17.3% of the initial length of 5.08 cm, a 56.2% reduction of area after fracture and Rockwell hardness of C 30.5.

A further specific preferred inventive steel, in the form of ingots 7.62 cm square and bar 2.54 cm square, was subjected to physical examination. The chemical composition of the steel is as follows: carbon 0.12%, chromium 12.0%, nickel 0.15%, molybdenum 0.06%, niobium-tantalum 0.15%, vanadium 0.25%, nitrogen 0.070% and the rest mainly iron. The physical properties of this steel, converted into standard test bars from an ingot 7.62 cm square or a bar 2.54 cm square under various conditions of quench hardening (982°C, 1038°C or 1093°C) with tempering at 593°C, 621°C or 649°C, are stated in Table V below.

Table V

Physical properties of hardened, tempered stainless 12 Cr steels which contain niobium-tantalum, vanadium and nitrogen						
Cross-section	State (°C)	Tensile strength (kg/cm ²)	0.2 limit (kg/cm ²)	Elongation after fracture (% of the initial length = 5.08 cm)	Reduction of area after fracture (% of the original cross-section)	Charpy notched bar impact strength (mkg)
Ingot (7.62 cm) ²	H-982; T-621	10335	9210	17	58	2.8/3.0
Ingot (7.62 cm) ²	H-982; T-649	9773	8648	16	59	4.7/5.7
Ingot (7.62 cm) ²	H-1038; T-621	10616	9351	16	59	3.0/3.0
Ingot (7.62 cm) ²	H-1038; T-649	10195	8999	16	60	3.5/4.1
Ingot (7.62 cm) ²	H-1093; T-621	10968	9702	16	58	2.5/2.5
Ingot (7.62 cm) ²	H-1093; T-649	10546	9351	15	58	2.9/3.5
Bar (2.54 cm) ²	H-982; T-593	11249	9843	16	58	3.0/4.0
Bar (2.54 cm) ²	H-982; T-621	10757	9491	16	55	2.5/3.0
Bar (2.54 cm) ²	H-1038; T-593	11460	9913	16	58	2.4/2.4
Bar (2.54 cm) ²	H-1038; T-621	10616	9281	17	58	2.5/2.5

H = Hardened by quenching at the temperature stated in °C

T = Tempered at the temperature stated in °C

Only very minor differences appear to be present in a comparison of the physical properties of a specimen made from a 7.62 cm square ingot with those made from a 2.54 cm square bar. Although the specimen made from a 7.62 cm square ingot, hardened by quenching at 982°C and tempered at 621°C, has a lower strength than that made from a 2.54 cm square bar similarly quench hardened and tempered, it has somewhat better deformability and impact resistance of 2.8/3.0 mkg compared to 2.5/3.0 mkg. With the exception of impact resistance, the physical properties are mainly identical at the somewhat higher quenching temperature of 1038°C with tempering at 621°C. The impact resistance is better in the specimen from the 7.62 cm² ingot, namely 3.0 mkg, whilst the specimen made from the 2.54 cm square bar

produced a figure of 2.5 mkg.

A further preferred steel with a somewhat greater chromium content has the following composition: approximately 0.1 to 0.2% carbon, approximately 15% chromium, approximately 0.1 to 0.2% nitrogen, approximately 0.1 to 0.3% or preferably approximately 0.2% niobium-tantalum, approximately 0.2% to 0.6%, preferably 0.3 to 0.4% vanadium and the remainder principally iron only. The phosphorous, sulphur, silicon, and molybdenum-tungsten content are low. Four specific examples of this steel with a different carbon and chromium content are described below. Table VI shows the chemical analysis of the steels and Table VII the corresponding physical properties.

Table VI

Four stainless 15-Cr steels containing niobium-tantalum, vanadium and nitrogen										
{PRIVATE }Melt no.	C	Mn	P	S	Si	Cr	Ni	N	Nb	V
R 5304-1	0.098	0.89	0.008	0.018	0.21	14.96	0.22	0.13	0.21	0.44
R 5304-2	0.13	0.89	0.008	0.018	0.21	14.96	0.22	0.13	0.21	0.44
R 5305-1	0.10	0.92	0.011	0.015	0.26	14.77	0.16	0.13	0.19	0.33
R 5305-2	0.14	0.92	0.011	0.015	0.26	14.77	0.16	0.13	0.19	0.33

The physical properties of the steels from Table VI in their hardened and tempered state (30 minutes heating to 1093°C and quenching with oil, followed by heating to 621°C for four hours and cooling with air, or hardening in the same way with subsequent tempering at 649°C for four hours and cooling with air, are stated in Table VII below.

Table VII

Physical properties of hardened, tempered stainless 15 Cr steels from Table VI					
Melt no.	State 1093°C/30 min/oil- quenched +x°C/4h/air cooled	Tensile strength (kg/cm ²)	0.2 limit (kg/cm ²)	Elongation after fracture (% of the initial length = 5.08 cm)	Reduction of area after fracture (% of the original cross-section)
R 5304-1	x °C = 621°C	10813	8824	13	33
R 5304-2	x °C = 621°C	11868	9843	13	36
R 5305-1	x °C = 621°C	11334	9393	15	51
R 5305-2	x °C = 621°C	12037	9906	9	18
R 5304-1	x °C = 649°C	10518	8690	15	47
R 5304-2	x °C = 649°C	11073	9140	14	48
R 5305-1	x °C = 649°C	10736	8950	13	41
R 5305-2	x °C = 649°C	11080	9288	15	49

The comparison of the physical properties of the steel with 15% chromium (melts R 5304-2 and 5305-2), shown in Table VII, with those of the steel with 12% chromium and the same carbon content, shown in Table V, shows the considerable improvement in tensile strength and yield point in the steel with 15% chromium, which, however, is achieved at the expense of a certain loss of deformability. Nevertheless, the principal advantage achieved with the steel with the higher chromium content is improved resistance to corrosion.

It is evident that this invention makes a stainless steel hardenable by quenching available, with which various objects mentioned above and many practical advantages may be achieved. The steel is comparatively cheap, as it contains only the minimum quantity of expensive alloys, but nonetheless possesses a combination of good tensile strength, yield point and ductility. The steel responds well to rolling and can easily be worked to make the widest variety of artifacts by various methods of forming, cutting, soldering and welding. The steel and the artifacts made from it are suitable for use in the quench hardened or quench hardened and tempered state.

PATENT CLAIM I

Stainless steel hardenable by heat treatment, characterized in that it contains 0.01 to 0.25% carbon, 10 to 16% chromium, 0.04 to 0.2% nitrogen and 0.03 to 0.75% niobium and tantalum.

SUB-CLAIMS

1. Steel in accordance with patent claim I, characterized in that it consists of 0.01 to 0.25% carbon, 0.01 to 3% manganese, 0.01 to 2% silicon, 10 to 16% chromium, whereby any molybdenum present does not exceed 0.3% and any tungsten present does not exceed 0.5%, and the total aggregate content of molybdenum and tungsten does not exceed 0.5%, and also of 0.04 to 0.2% nitrogen and 0.03 to 0.75% niobium and tantalum, at least the greater proportion of the remainder being iron.
2. Steel in accordance with patent claim I, characterized in that it consists of 0.01 to 0.25% carbon, 0.01 to 1% manganese, 0.01 to 1% silicon, 10 to 16% chromium, whereby the total aggregate content of molybdenum and tungsten does not exceed 0.2%, and also of 0.06 to 0.16% nitrogen, 0.03 to 0.75% niobium and tantalum, and up to 0.75% vanadium, at least the greater proportion of the remainder being iron.
3. Steel in accordance with patent claim I, characterized in that it consists of 0.01 to 0.25% carbon, 10 to 16% chromium, whereby any molybdenum present does not exceed 0.3% and any tungsten present does not exceed 0.5%, and the total aggregate content of molybdenum and tungsten does not exceed 0.5%, and also of 0.04 to 0.16% nitrogen, 0.03 to 0.75% niobium and tantalum and 0.03 to 0.35% vanadium, at least the greater proportion of the remainder being iron.
4. Steel in accordance with patent claim I, characterized in that it consists of 0.05 to 0.25% carbon, 10 to 13% chromium, whereby any molybdenum present does not exceed 0.3% and any tungsten present does not exceed 0.5%, and the total aggregate content of molybdenum and tungsten does not exceed 0.5%, and also of 0.04 to 0.16% nitrogen, 0.1 to 0.75% niobium and tantalum and 0.2 to 0.4% vanadium, at least the greater proportion of the remainder being iron.

5. Steel in accordance with patent claim I, characterized in that it consists of 0.1 to 0.2% carbon, 11 to 12% chromium, whereby the total aggregate content of any molybdenum and tungsten present does not exceed 0.2%, and also of 0.1 to 0.16% nitrogen, 0.1 to 0.3% niobium and tantalum and 0.1 to 0.4% vanadium, at least the greater proportion of the remainder being iron.
6. Steel in accordance with patent claim I, characterized in that it consists of 0.1 to 0.2% carbon, 13 to 15% chromium, whereby any molybdenum present does not exceed 0.3% and any tungsten present does not exceed 0.5%, and the total aggregate content of molybdenum and tungsten does not exceed 0.5%, and also of 0.04 to 0.2% nitrogen, 0.1 to 0.3% niobium and tantalum and 0 to 0.6% vanadium, at least the greater proportion of the remainder being iron.
7. Steel in accordance with patent claim I, characterized in that it consists of 0.1 to 0.2% carbon, 15% chromium, whereby the total aggregate content of any molybdenum and tungsten present does not exceed 0.5%, and also of 0.1 to 0.2% nitrogen, 0.1 to 0.3% niobium and tantalum and 0.2 to 0.6% vanadium, at least the greater proportion of the remainder being iron.
8. Steel in accordance with patent claim I in the form of bar and structural shaped steel, characterized in that it consists of 0.01 to 0.25% carbon, 10 to 16% chromium, whereby the total aggregate content of any molybdenum and tungsten present does not exceed 0.15%, and also of 0.04 to 0.2% nitrogen, 0.03 to 0.75% niobium and tantalum, and 0.03 to 0.75% vanadium, at least the greater proportion of the remainder being iron.
9. Steel in accordance with patent claim I characterized in that it contains up to 0.75% vanadium.
10. Steel in accordance with patent claim I or one of the preceding sub-claims, characterized in that it does not contain more than 0.3% molybdenum, not more than 0.5% tungsten and not more than an aggregate of 0.5% of molybdenum and tungsten.

PATENT CLAIM II

Use of a steel in accordance with patent claim I to produce turbine and compressor blades, characterized in that the blades are made of a steel which consists of 0.01 to 0.25% carbon, 0.01 to 3% manganese, 0.01 to 2% silicon, 10 to 13% chromium, 0.04 to 0.16% nitrogen and 0.03 to 0.75% niobium and tantalum, at least the greater proportion of the remainder being iron.

SUB-CLAIM

11. Use in accordance with patent claim II, characterized in that the blades are made of a steel which contains not more than 0.3% molybdenum, not more than 0.5% tungsten and an aggregate of not more than 0.5% molybdenum and tungsten.

Note by the Federal Office for Intellectual Property:

Should parts of the description not match the definition of the invention stated in the patent claim, it is declared that the patent claim is crucial to the substantive scope of validity of the patent, under Article 51 of the [Swiss] Patents Act.